



Validation of Ogawa passive samplers for the determination of gaseous ammonia concentrations in agricultural settings

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Abstract

The Ogawa passive sampler (Ogawa USA, Pompano Beach, Florida) is a useful tool for monitoring atmospheric ammonia ($\text{NH}_3(\text{g})$) concentrations and assessing the effects of agricultural waste management practices on $\text{NH}_3(\text{g})$ emissions. The Ogawa sampler, with filter-discs impregnated with citric acid, was used to trap and determine $\text{NH}_3(\text{g})$ concentrations in a variety of agricultural settings. A wide range of $\text{NH}_3(\text{g})$ concentrations can be monitored by varying the sampler exposure time, provided that no more than $\sim 10 \mu\text{g}$ of $\text{NH}_3\text{-N}$ are adsorbed on the acid-coated filters. Concentrations less than $1 \mu\text{g NH}_3\text{-N m}^{-3}$ can be detected using long deployments (≤ 14 days), while concentrations as great as $10 \text{ mg NH}_3\text{-N m}^{-3}$ may be determined in very short (e.g. 5 min) deployments. Reproducibility ranged from 5% to 10% over the range of concentrations studied and passive determinations of $\text{NH}_3(\text{g})$ were similar to those determined using dilute-acid gas scrubbers.

Background levels of $\text{NH}_3(\text{g})$ at a non-agricultural site in southern Delaware were typically $< 1 \mu\text{g NH}_3\text{-N m}^{-3}$. The air entering a chicken house was $10 \mu\text{g NH}_3\text{-N m}^{-3}$, reflecting the background levels in agricultural settings in this region. Within the house, concentrations $\leq 8.5 \text{ mg NH}_3\text{-N m}^{-3}$ were observed, reflecting the high rates of $\text{NH}_3(\text{g})$ emission from chicken excreta. Using measured $\text{NH}_3(\text{g})$ concentrations and poultry house ventilation rates, we estimate that each broiler grown to production size over 6 weeks contributes approximately $19 \pm 3 \text{ g}$ of $\text{NH}_3\text{-N}$ to the atmosphere, a value consistent with other published results.

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1. Introduction

Direct deposition of atmospheric nitrogen (N) compounds to land surfaces and water bodies is increasingly recognized as a significant contribution to ecosystem degradation via eutrophication and/or acidification (e.g.

Jaworski et al., 1997; Paerl et al., 2002). Deposition of atmospheric nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), gaseous ammonia ($\text{NH}_3(\text{g}) = \text{NH}_3^0$), and organic nitrogen (R-N) can impact ecosystem health and function. Of the biologically available forms, the least is known about the sources, transport, and deposition of $\text{NH}_3(\text{g})$ and R-N. In regions with extensive animal production facilities, $\text{NH}_3(\text{g})$ has been shown to be a significant component of atmospheric N deposition to sensitive terrestrial, aquatic, and marine ecosystems (Chimka et al., 1997; Fowler et al., 1998a; Walker et al., 2000). In order to properly assess the role of atmospheric N on ecosystem function and stability in these regions, more information is needed concerning

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the sources, transport, and deposition of gaseous ammonia (Bouwman et al., 1997; Chesapeake Bay Program, 2001; Aneja et al., 2001).

1.1. Sources of atmospheric ammonia

Agricultural activities, in particular animal husbandry, are the dominant source of $\text{NH}_3(\text{g})$ emissions to the atmosphere, contributing an estimated 90% of the total in Western Europe (Sutton et al., 1995; Kirchmann et al., 1998) and the US (Battye et al., 1994). Poultry production can be a significant source of $\text{NH}_3(\text{g})$, with about one-half of the total emissions estimated to arise from housing and one-half from land application of waste litter (Pain et al., 1998). The rates of $\text{NH}_3(\text{g})$ production and emission from a particular agricultural site are dependent on growing conditions (e.g. diet, ventilation regime), waste handling practices (e.g. frequency of clean-out, litter amendments), and local meteorological conditions (e.g. temperature, humidity, wind). Other anthropogenic sources of $\text{NH}_3(\text{g})$ (e.g. motor vehicles, waste processing, industrial refrigeration, etc.) are thought to provide only a small contribution (Battye et al., 1994). Non-agricultural sources, however, are difficult to quantify due to the large number of sources, both fixed and mobile, and the lack of reliable emission data under “real-world” conditions (Sutton et al., 2000).

1.2. Ammonia in the environment

Atmospheric $\text{NH}_3(\text{g})$ has a relatively short atmospheric lifetime, ranging from a few hours to 5 days (Chimka et al., 1997) because it can be adsorbed by water, react with acid gases (NO_x or SO_x) to produce aerosols, or be dry-deposited locally to vegetation, soil, or water surfaces (ApSimon et al., 1987; Scudlark and Church, 1999). Ammonia that is converted to aerosols has a lower reactivity, a longer residence time (5–10 days), can be dispersed over greater distances, and is removed primarily by wet deposition (Chimka et al., 1997; Scudlark and Church, 1999). On deposition, ammonia contributes to acidification, reduction of species diversity, and eutrophication in natural ecosystems.

Ammonia can also directly affect livestock health and productivity and the health of farm workers regularly exposed to high levels of $\text{NH}_3(\text{g})$. Elevated ammonia levels in poultry houses have been linked to poultry respiratory disorders (Anderson et al., 1964; Nagaraja et al., 1983) and to decreased growth rates (Reece et al., 1980). Within poultry facilities, $\text{NH}_3(\text{g})$ concentrations are controlled by ventilation and litter treatments. $\text{NH}_3(\text{g})$ has a sharp and irritating odor and the European exposure limits for human health are $22 \text{ mg NH}_3\text{-Nm}^{-3}$ ($35 \mu\text{l l}^{-1}$) for a 10 min exposure and

$16 \text{ mg NH}_3\text{-Nm}^{-3}$ ($25 \mu\text{l l}^{-1}$) for an 8 h exposure (Shah, 1997).

1.3. Techniques for $\text{NH}_3(\text{g})$ determination

A number of techniques have been used for the determination of $\text{NH}_3(\text{g})$ in the atmosphere. These methods include direct chemiluminescence (Demmers et al., 1998), filtration packs (Sickles et al., 1999), denuders (Leuning et al., 1985), and gas scrubbers (Fehsenfeld, 1995), and generally show good agreement.

Passive samplers of gaseous compounds are finding increased environmental application (Willems and Hofschreuder, 1990; Krupa and Legge, 2000; Rabaud et al., 2001; Hagenbjörk-Gustafsson et al., 2002; Tate, 2002; Thöni et al., 2003). In passive samplers, the atmospheric compound of interest diffuses to a reactive surface, which chemically traps the gas. Compared with conventional methods, passive samplers are less expensive, can be deployed unattended for extended periods, and do not require electricity. Thus, passive samplers can be deployed in larger numbers and over a wider area for monitoring and modeling of the sources, distribution, and fate of gases in the environment. While the Ogawa sampler has been successfully used for the determination of a variety of gaseous species, such as NO , NO_2 , NO_x , O_3 , SO_2 , and NH_3 (Koutrakis et al., 1993; Liu et al., 1994; Liu et al., 1995; Varnes et al., 1999; Krupa and Legge, 2000; Tate, 2002; Thöni et al., 2003), its efficacy for the determination of $\text{NH}_3(\text{g})$ has not been well established, particularly over the wide range of concentrations found in agricultural areas.

In this study, we evaluate the Ogawa passive sampler for the determination of $\text{NH}_3(\text{g})$ concentrations in a poultry-producing region and at a nearby background site. The sensitivity and reproducibility of the sampler were assessed and its accuracy was evaluated by comparison with a commonly used gas scrubber method. The data were employed to derive a preliminary estimate of $\text{NH}_3(\text{g})$ emissions from local poultry operations.

2. Methods

2.1. Description of samplers

Ogawa passive samplers (Ogawa USA, Inc., Pompano Beach, Florida, ogawausa.com; Fig. 1) were used to determine the time-averaged concentrations of $\text{NH}_3(\text{g})$ in and around poultry houses, at other sites in agricultural settings, and at a background reference site (National Acid Deposition Program—NADP—site at Cape Henlopen State Park, Lewes) in southern

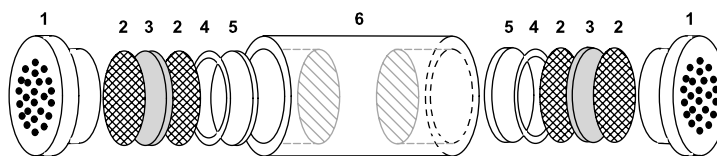


Fig. 1. Components of the Ogawa Passive Sampler. The sampler body (6) is 2 cm (outer diameter) \times 3 cm (length) and has two independent cavities (1.4 cm inner diameter) each containing a diffusive-barrier end-cap (1), a reactive filter (3) between an inner and outer stainless steel screen (2), and a retainer ring (4) over a base pad (5). See ogawausa.com for additional design and deployment details.

Delaware. The samplers consist of a solid Teflon cylinder with two open, but unconnected ends, each containing a reactive glass-fiber filter impregnated with citric acid (see below). The filter is mounted between two stainless steel screens (0.152 cm^2 open area, 0.02 cm thick), situated behind a diffusion-barrier end-cap containing 25 holes (open area of 0.785 cm^2 , 0.6 cm thick). The two filters can be sampled independently for the purpose of replication, but in this study both were combined for a single analysis.

2.2. Preparation of the sampler

The disassembled components of the passive sampler were thoroughly cleaned prior to each use (to avoid contamination and carryover) by soaking overnight in 5% (w/v) citric acid, rinsing thoroughly with deionized water (ASTM Type I), and drying under a specially prepared clean bench (see below). The glass-fiber filters (14 mm, #30 grade, Schleicher and Schuell) were cleaned by soaking overnight in the 5% citric acid solution, followed by copious rinses with 5% citric acid, deionized water, and methanol on a fritted 25 mm filter-base, employing gentle aspiration.

The components were assembled into the sampler using clean forceps. First, a cleaned filter was loaded in the sampler on the bottom screen, and once dry (5–10 min), was impregnated with 100 μl of 2% (w/v) citric acid-2% (v/v) glycerin in methanol. The impregnating solution was allowed to evaporate slightly (2–5 min) until just damp, to avoid distributing the solution onto other parts of the apparatus. The top screen and endcap were then inserted on top of the impregnated filter. The process was then repeated for the other end of the sampler. The prepared samplers were frozen in individual air-tight vials in a larger air-tight container until deployment.

The handling of filters and sample manipulation were carried out in a “Class 100” clean bench, specially equipped with an ammonia scrubber (fiberglass pre-filter sprayed before each use with 5% citric acid) using “clean” techniques. Clean latex gloves were used when handling samplers. Exposure of materials, samplers, and reagents to ambient air was minimized to avoid

potential contamination from commercial cleaning solutions, cigarette smoke, and organic waste materials.

2.3. Sampler deployment

The samplers were deployed using a PVC rain shelter and support clips provided by the manufacturer (see ogawausa.com) for intervals ranging from 5 min to 14 days, depending on the anticipated concentration of $\text{NH}_3(\text{g})$. Even in the absence of rain, the shelter is required to minimize dust contamination and the effects of advection on the diffusive samplers. Prepared samplers were transported to and from the field on ice, in air-tight containers, and minimally handled in the field using latex gloves. Upon retrieval, the exposed samplers were frozen until analysis. No effect of frozen storage, either prior to (≤ 10 days) or after (≤ 14 days) exposure, was observed.

2.4. Analysis

The filters were transferred (using forceps) to acid-washed glass vials containing 8.0 ml of deionized water. The vials were sonicated for 10 min, and the extract was filtered through a 13-mm diameter, 0.2- μm Acrodisc[®] in-line filter using a 10 ml syringe. The syringe and filter were prerinsed with deionized water and 1–2 ml of sample. Filtering removes glass-fiber filter particles, which cause a positive absorbance artifact during analysis.

While a number of acids have been used for $\text{NH}_3(\text{g})$ adsorption in denuders and passive samplers (e.g. citric, oxalic, tartaric, sulfuric and phosphoric), we used citric acid due to its chemical compatibility with the colorimetric method of NH_4^+ analysis (see below). Rabaud et al. (2001) report no difference in response or performance consistency between acids for a similar sampler. Tests in our laboratory revealed no significance difference between the use of dilute phosphoric and citric acids.

The ammonium citrate extract was analyzed using segmented-flow colorimetry by the phenol-hypochlorite method (Solorzano, 1969) and employing an O/I Analytical Flow Solutions IV analyzer.

2.5. Calculations

The flux of $\text{NH}_3(\text{g})$ from the ambient atmosphere to the reactive surface of the Ogawa sampler, J (mass $\text{area}^{-1} \text{ time}^{-1}$), is described, at steady-state, by Fick's Law:

$$J = D_B \frac{\Delta C}{\Delta x}, \quad (1)$$

where D_B is bulk gas diffusion coefficient, Δx is the diffusional distance through the sampler, and ΔC is the difference between the average ambient concentration (C_A) and the concentration at the reactive surface (C_S). The mass load of $\text{NH}_3(\text{g})$ that accumulates on a filter, M , is a function of deployment time, t , the effective x -sectional area open to diffusion, A , and the flux, J :

$$M = JAt = D_B A t \frac{\Delta C}{\Delta x}. \quad (2)$$

Since, A and D_B can be determined from the geometry of the sampler and $C_S = 0$ (due to rapid and complete gas trapping), C_A can be directly related to M and t :

$$\frac{M}{t} = JA = \left(\frac{D_B A}{\Delta x} \right) C_A = m_B C_A, \quad (3)$$

where $m_B = (D_B A / \Delta x)$ is the "mass transfer coefficient" or "sampling rate" for the sampler.

The mass transfer coefficient, m_B , is dependent on the geometry of the sampler's diffusive pathways and the molecular diffusivity of the $\text{NH}_3(\text{g})$, $D_{\text{NH}_3}(T)$. Massman (1998) reviewed the limited experimental data for D_{NH_3} as a function of temperature (K) at 1 atm pressure and reported:

$$D_{\text{NH}_3}(T) = 0.1987 \left[\frac{T}{273.15} \right]^{1.81}. \quad (4)$$

The estimated precision of $D_{\text{NH}_3}(T)$ is approximately $\pm 9\%$, within the range of normal atmospheric temperatures, which limits the overall accuracy of the sampler. At 25°C , $D_{\text{NH}_3} = 0.232 \text{ cm}^2 \text{ s}^{-1}$ and this value, which falls within the range of the uncertainty of $D_{\text{NH}_3}(T)$ over the temperature interval of $11\text{--}39^\circ\text{C}$, was used throughout this study.

To reach the reactive filter, $\text{NH}_3(\text{g})$ diffuses through the diffusive-barrier end-cap and outer screen. By analogy to laminated solids (Crank, 1975, p. 273), the bulk m_B is related to the component mass transport coefficients for the end-cap (m_{DBEC}) and the screen (m_{OS}) as follows:

$$\frac{1}{m_B} = \frac{1}{m_{\text{DBEC}}} + \frac{1}{m_{\text{OS}}}. \quad (5)$$

In this equation, m_{DBEC} and m_{OS} are calculated independently from the thickness (Δx) and open area of each barrier (A) using the relationship given in Eq. (3). For $\text{NH}_3(\text{g})$ at 25°C and the Ogawa sampler, m_B for each side of the sampler is $15.5 \text{ cm}^3 \text{ min}^{-1}$ or, for

both sides of the sampler, $31.1 \text{ cm}^3 \text{ min}^{-1}$. This latter value is used throughout this study and is appropriate as long as the diffusional geometry of sampling remains constant (see below).

2.6. Field deployments

Blanks and reproducibility. The field blank was a loaded sampler taken to and from the field with other samplers but never removed from its air-tight vial. The laboratory/filtration blank remained frozen in the laboratory until analyzed. Both of these blanks were prepared and processed at the same time and in the same way as the deployed samplers to determine if contamination occurred during the sampler loading, transport, or analysis. A reagent blank, consisting of $200 \mu\text{l}$ of citric acid in 8 ml of distilled water, was analyzed to determine the background reagent contamination.

To determine reproducibility, replicate sampling was performed over a range of sampling times and ammonia concentrations, from the regional background to the high levels in and around poultry production facilities. The replicates were deployed within 0.3 m of each other and for the same time interval. Reproducibility reflects the uncertainty in sampling, sample handling, analysis, and small-scale variability for typical deployments.

Intercomparison studies. On a number of occasions, the passive samplers were deployed within 0.3 m of a $\text{NH}_3(\text{g})$ scrubber of a design described by Meisiniger et al. (2001). The $\text{NH}_3(\text{g})$ scrubber consisted of a glass gas-washing bottle containing 80 ml of 2 mM phosphoric acid and equipped with a 12 mm extra-coarse frit. A vacuum pump and thermal flowmeter connected downstream of the scrubber drew air through the acid solution at a flow rate of $4\text{--}5 (\pm 0.05) \text{ l min}^{-1}$, trapping $\text{NH}_3(\text{g})$ as NH_4^+ . Samples were analyzed without filtration using the same method as for the passive samplers.

Saturation and deployment time limitations. On two occasions, a series of samplers were deployed adjacent to each other in an active poultry house, for time intervals from 5 min to 4 days , to determine the mass loading and optimum deployment time for the samplers under high $\text{NH}_3(\text{g})$ conditions where the limitations of Eq. (3) could be evaluated.

Concentrations in and around a poultry production facility. Inside a chicken house, the samplers were deployed for $\leq 2 \text{ h}$ within 1.3 m of the sidewall ventilation fans and 1.3 m from the floor (about mid-height of the fans). The ventilation rate of the house was determined from the rated discharge of the operating ventilation fans ($9000 \text{ ft}^3 \text{ min}^{-1}$ for the sidewall fans; $17000 \text{ ft}^3 \text{ min}^{-1}$ for tunnel fans) corrected for the estimated efficiency of the fans and the monitored fraction of time that the fans were in use during sampling. The radially integrated discharge of two

sidewall fans was determined using a thermal anemometer and the calculated efficiency ($87 \pm 16\%$) of these fans was used for all ventilation determinations. During sidewall fan operation, the discharge of $\text{NH}_3(\text{g})$ from the house was determined as a product of the average $\text{NH}_3(\text{g})$ concentration within the house and the total ventilation rate. During tunnel fan operation, the discharge of $\text{NH}_3(\text{g})$ was determined as the product of the estimated ventilation rate and the concentration of $\text{NH}_3(\text{g})$ measured closest to the fan.

To determine the spatial variability of $\text{NH}_3(\text{g})$ concentration around the house during tunnel fan operation. Samplers were deployed at the intake (opposite the tunnel fans) and exhaust (adjacent to the tunnel fans) ends, and along both sides of the house, 1.5 m above the ground and 1.8 m from the house. To determine how rapidly exhausted $\text{NH}_3(\text{g})$ concentrations were reduced by dispersion and/or deposition outside of the house, an array of 4–8 samplers were deployed along perpendicular transects away from the operating sidewall fans at a height of 1.5 m.

3. Results and discussion

3.1. Validity of samplers

Blanks and reproducibility. Using the stringent cleaning and handling protocols outlined above, it was possible to maintain the field blanks at a low and consistent level of $297 \pm 82 \text{ ng NH}_3\text{-N}$ ($n = 44$; all uncertainties are reported at the 1σ level). The laboratory/filtration blank contributed $113 \pm 55 \text{ ng NH}_3\text{-N}$ ($n = 20$), of which $49 \pm 7 \text{ ng NH}_3\text{-N}$ ($n = 20$) was provided by the reagents.

The detection limit for the sampler, defined as 2σ of the field blank, is thus $164 \text{ ng NH}_3\text{-N}$. This limit dictates a minimum deployment time for sampling low $\text{NH}_3(\text{g})$ concentrations (Fig. 2). For example, the detection limit is $3.7 \mu\text{g NH}_3\text{-N m}^{-3}$ for a 1-day deployment and $0.26 \mu\text{g NH}_3\text{-N m}^{-3}$ for a 14-day deployment. The detection limit might be further improved by longer deployments (> 14 days) but this was not investigated. Under background conditions at the NADP site, where the concentration and variability of the field blanks could be better controlled, significantly lower detection limits were observed ($\sim 50 \text{ ng NH}_3\text{-N}$). The overall reproducibility of the protocol was 5–10% between the detection and saturation limits (see below), as estimated from the relative standard deviation of replicated deployments.

Saturation and deployment times. In two studies in a chicken house, the accumulated mass load of $\text{NH}_3(\text{g})$ on reactive filters was not linear with time (Fig. 3). A maximum apparent atmospheric concentration is reached within less than 1 h when the mass load of $\text{NH}_3(\text{g})$ on the sampler exceeds $10 \mu\text{g NH}_3\text{-N}$. After this

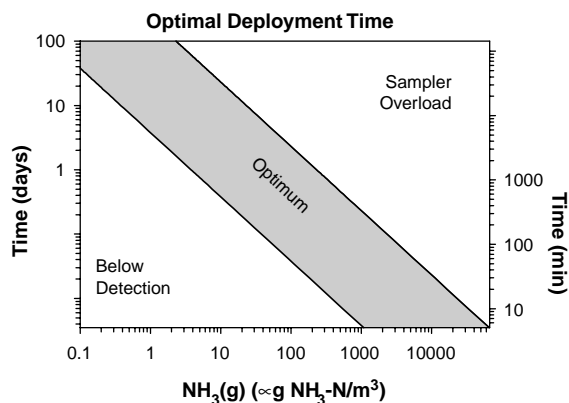


Fig. 2. The sampler deployment time is constrained by the ambient concentration, the detection limit of the sampler, and the “saturation” level at which the sampler no longer reliably estimates the ambient $\text{NH}_3(\text{g})$. Also, deployment times $< 5 \text{ min}$ are generally impractical, due to the uncertainty associated with sample handling and imprecise deployment and retrieval times. The optimal operation range is stippled.

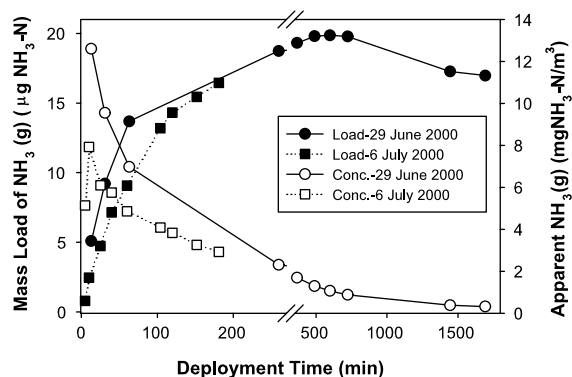


Fig. 3. Mass load, apparent concentration, and saturation of the Ogawa sampler. The mass transfer coefficient and the mass-loading rate decrease with time. Overloading of the sampler leads to a non-linear relationship between the ambient concentration and mass loading that restricts the deployment time and concentration over which the Ogawa sampler may be reliably used to estimate $\text{NH}_3(\text{g})$.

time, an erroneous apparent concentration is determined due to a decrease in m_B (Eqs. (3) and (5)). In the 29 June study there is evidence, in addition, that at high filter loads adsorbed NH_4^+ decreases with time, due to oxidation, volatilization, or other reactions that prevent detection during subsequent analysis. Therefore, sampler saturation imposes an upper limit to deployment times and measurable $\text{NH}_3(\text{g})$ concentrations, as shown in Fig. 2.

The apparent saturation of the samplers at mass loadings above $10 \mu\text{g NH}_3\text{-N}$ is not due to chemical

exhaustion of the citrate reactant. $\text{NH}_3(\text{g})$ reacts with citric acid to form $\text{NH}_4\text{H}_2\text{C}_6\text{H}_5\text{O}_7$, $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$, or $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$. The stoichiometric capacity of the sampler should therefore be 290–875 $\mu\text{g NH}_3\text{-N}$. The apparent saturation limit, 10 $\mu\text{g NH}_3\text{-N}$, represents only 1–3% of the sampler capacity, which is similar to the 8% saturation limit reported for a different passive sampler design (Leuning et al., 1985). Saturation is probably due to a change in the mass transfer rate of the sampler: once the filter surface has fully reacted with $\text{NH}_3(\text{g})$, subsequent gas molecules must penetrate through a thickening reacted surface to the unreacted zone below. Under these conditions, the constant geometry (and constant m_B) needed to apply Eq. (3) is no longer valid and the sampling rate of the Ogawa sampler will drop.

The best way to avoid the effective saturation of the reactive filter is to keep the overall mass loading below the level that leads to non-steady mass transfer. Fig. 2 summarizes the optimal operating range of the Ogawa sampler as a function of $\text{NH}_3(\text{g})$ concentration and deployment time, considering both the observed detection limit and saturation level.

Comparison with a reference method. The results of the simultaneous deployments of passive samplers and scrubbers (Fig. 4) show a close agreement between the two methods. The relative uncertainties in duplicated passive sampler measurements are shown. The uncertainty of scrubbers was about $\pm 5\%$, but is based on limited replications ($n = 3$). Over a broad range of concentrations, the passive samplers yield comparable results to those determined by the scrubber reference method. This demonstrates that the Ogawa passive samplers are a viable alternative to other $\text{NH}_3(\text{g})$ -sampling methods.

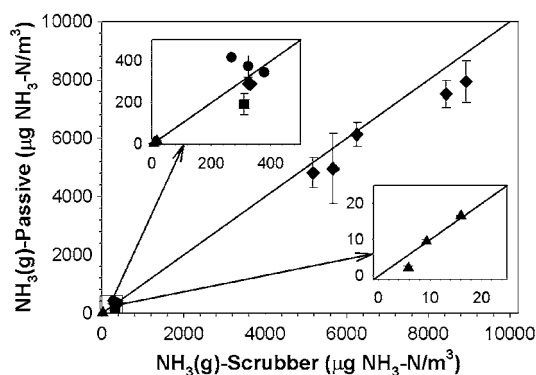


Fig. 4. Comparison of results obtained with the Ogawa passive sampler and ammonia trapped in gas scrubbing bottles. The results indicate that Ogawa passive samplers can reliably determine $\text{NH}_3(\text{g})$ concentrations over a wide range of concentrations. Deployment times were <1 h (●), 1–2 h (◆), 6 h (■), and 3–5 days (▲).

The largest systematic differences between the samplers were found at the highest concentrations found in a dusty poultry house. The Ogawa samplers determine only $\text{NH}_3(\text{g})$ while the scrubbers determine both $\text{NH}_3(\text{g})$ plus some fine-particulate NH_x ($=\text{NH}_3 + \text{NH}_4^+$). Most of the atmospheric NH_x at our sites would be expected to be in the gaseous phase, but in the poultry house, NH_x in litter dust may have contaminated the scrubbers (Fig. 4) resulting in the observed differences.

3.2. $\text{NH}_3(\text{g})$ in and around poultry houses

Ammonia measurements were made at different times of the year and different stages of the poultry production cycle. The houses were of a tunnel design that permits outside ventilation through the inlet end of the house and/or through roof-top ventilation boxes. Sidewall ventilation predominates during the early weeks of a typical 6-week grow-out cycle, while tunnel fans are used toward the end of the cycle. Each house contained approximately 27,500 chickens, but was managed differently in terms of diet, ventilation, and heating schedules.

Ammonia concentrations outside one poultry house during tunnel fan operation (Fig. 5a) show low concentrations (7–10 $\mu\text{g NH}_3\text{-N m}^{-3}$) at the inlet end, which reflect background levels found in agricultural areas of southern Delaware (<1 to $\sim 15 \mu\text{g NH}_3\text{-N m}^{-3}$; Scudlark, 2002). This contrasts with the concentrations at the NADP site, which were generally $<1 \mu\text{g NH}_3\text{-N m}^{-3}$. The highest concentrations, 962–1175 $\mu\text{g NH}_3\text{-N m}^{-3}$, were those in air discharging from the poultry house. Intermediate levels, 34–60 $\mu\text{g NH}_3\text{-N m}^{-3}$, were

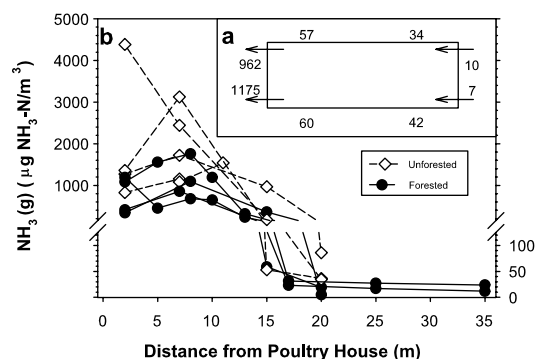


Fig. 5. Concentrations of $\text{NH}_3(\text{g})$ around chicken houses in Sussex County, Delaware. (a) In 10-h deployments, the lowest concentrations were found in the incident air to a house and the highest (which reflect lower bounds due to possible sampler saturation) were found downstream of the ventilation fans. (b) Concentrations after 24–29-h deployments perpendicular to the house when ventilation is through sidewall fans are high adjacent to the fan, but drop close to the agricultural background within 20 m of the sides of the house. The highest concentrations may reflect lower bounds due to sampler saturation.

Table 1
Concentrations, ventilation rates, and $\text{NH}_3(\text{g})$ discharge from a poultry house

Concentration ($\mu\text{g NH}_3\text{-N m}^{-3}$) (n)	Ventilation rate ($\text{m}^3 \text{s}^{-1}$)	$\text{NH}_3(\text{g})$ discharge (kg day^{-1})	Notes
8425 ± 732 (3)	7.3 ± 1.4	5.3 ± 1.1	14 September 2000; 3 sidewall fans; intermittent operation
7190 ± 420 (5)	14.8 ± 2.8	9.2 ± 1.8	23 September 2000; 4 sidewall fans; all fans on full time
$[1570\text{--}6255]^a$ (5)	40.9 ± 7.7^b	22.1 ± 4.7	6 October 2000; 6 tunnel fans; all fans on full time
Integrated daily discharge		12.2 ± 1.7	

^a Range given as concentrations increased systematically as the tunnel fans were approached. Highest value near the tunnel fans with 10% assumed uncertainty is used to calculate discharge.

^b Estimated from fan ratings ($17,000 \text{ ft}^3 \text{ min}^{-1}$; $8 \text{ m}^3 \text{ s}^{-1}$), assuming the same efficiency and uncertainty found from measurements made on sidewall fans.

found along the sides of the house and likely reflect wind dispersion of $\text{NH}_3(\text{g})$, local re-emission of $\text{NH}_3(\text{g})$ from previously deposited material, and/or contributions from nearby houses.

Ammonia-N concentrations along transects outside of the house (Fig. 5b) are high adjacent to the house ($330\text{--}4400 \mu\text{g NH}_3\text{-N m}^{-3}$), but rapidly fall back to concentrations only slightly above the agricultural background ($\leq 25 \mu\text{g NH}_3\text{-N m}^{-3}$) at distances beyond 20 m. Fowler et al. (1998b) similarly found that $\text{NH}_3(\text{g})$ concentrations fell to $23\text{--}63 \mu\text{g NH}_3\text{-N}$ at a distance of 15 m from a UK poultry house. Although there were some differences in the decline of $\text{NH}_3(\text{g})$ with distance from the house depending on whether there were nearby trees in addition to grassy vegetation, there is no way to uniquely attribute this decline to the effects of dispersion or deposition.

Ammonia concentrations were also measured within one broiler house several times during the 6-week grow-out cycle (Table 1). Concentrations were highest ($8425 \pm 732 \mu\text{g NH}_3\text{-N m}^{-3}$) early in the chicken grow-out cycle when the ventilation rates were lowest (to maintain optimal temperature for chicks). Later in the grow-out cycle, concentrations decrease as ventilation rates increased. However, the mass discharge of $\text{NH}_3(\text{g})$ to the environment increased with time as the birds were fed, grew, and excreted (Table 1).

The data of Table 1 can be used to estimate the integrated $\text{NH}_3(\text{g})$ emission over a typical 6-week grow-out cycle, assuming that each sample is representative of a 2-week period during the cycle. This calculation produces an integrated discharge estimate from this one house of $12.2 \pm 1.7 \text{ kg NH}_3\text{-N day}^{-1}$ (with the uncertainty reflecting both $\text{NH}_3(\text{g})$ determinations and ventilation rates). For a house containing 27,500 chickens this discharge amounts to $19 \pm 3 \text{ g NH}_3\text{-N bird}^{-1}$ for the grow-out cycle. This estimate is consistent with $\text{NH}_3(\text{g})$ emission factors previously reported for poultry litter systems ($15\text{--}25 \text{ g NH}_3\text{-N bird}^{-1} \text{ cycle}^{-1}$; Battye et al., 1994; Phillips et al., 1995; Sutton et al., 1995; Wathes et al., 1997; Van der Hoek, 1998).

There are several uncertainties associated with this preliminary estimate of $\text{NH}_3(\text{g})$ emissions from poultry production beyond the uncertainty in $\text{NH}_3(\text{g})$ concentrations and ventilation rates. These include the lack of measurements of residual fluxes from old litter in the house and the use of instantaneous (rather than integrated) measurements, which do not reflect changing feeding rations and ventilation rates. Finally, there are a wide range of chicken-house designs and poultry management practices which will require more extensive sampling to develop more precise estimates of ammonia emissions from poultry production in southern Delaware.

4. Summary

The above results show that the Ogawa sampler can be successfully deployed to estimate atmospheric $\text{NH}_3(\text{g})$ concentrations over a wide range of conditions. The low cost, low operating requirements, and good agreement with traditional sampling techniques indicate that the Ogawa passive sampler is an excellent alternative to the other methods for determining $\text{NH}_3(\text{g})$ and could find wide application in environmental monitoring studies. The Ogawa samplers have some limitations when sampling extremely high or extremely low $\text{NH}_3(\text{g})$ concentrations. These limitations can be overcome by controlling the deployment time of the sampler to ensure that quantifiable amounts of ammonia are collected.

The Ogawa passive samplers were successfully used to determine the $\text{NH}_3(\text{g})$ concentrations in and around poultry production houses in order to test the sampler and obtain preliminary estimates of $\text{NH}_3(\text{g})$ fluxes to the atmosphere. The Ogawa samplers, because of their ease of deployment and wide operational range, could provide the basis for evaluating management practices aimed at reducing $\text{NH}_3(\text{g})$ emissions from animal production facilities. Improving $\text{NH}_3(\text{g})$ management in broiler production could result in both economic benefits to the farmer and environmental benefits to the watershed.

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